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Permeability of Soils to Four Organic Liquids and Water

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ABSTRACT

Saturated hydraulic conductivities and intrinsic permeabilities were evaluated for eight contrasting soils with four organic liquids and water. The organic liquids were kerosene, ethylene glycol, isopropyl alcohol and xylene. Intrinsic permeability for any given soil varied inversely with the dielectric coefficient -- water gave the lowest value. The mechanism is apparently related to the double-layer phenomena with water leading to the most dispersed system. A multiple regression analysis related intrinsic permeability to silt, dielectric coefficient, clay and bulk density with a goodness of fit (R) of 0.74. An analysis of all the non-aqueous liquids, with water permeability as a dependent variable, resulted in an R of 0.84. The study has relevance with regard to movement of such organics in soils either as a pollutant or as a solvent carrying pollutants.

INTRODUCTION

Safe disposal of toxic wastes is of concern throughout the developed countries. Improper disposal of organic liquid plays a significant role in the spreading of wastes, often endangering ground waters. Both the liquids themselves and dissolved materials are of relevance. In addition to the local hydrology, the reactivity of these materials with soils determine their potential hazard. Most studies of mechanisms on migration rates of metals through soils ([1], [2], [3]) are for aqueous systems only, although others have evaluated specific organic solvents in a mixed phase with water ([4], [5]; [6]). Brown and Anderson [7] and Anderson and Brown [8] discuss mobility of aqueous solutions and organic solvents through clay liners and failure mechanisms of clay liners. They conclude that compared to water, "clay liners showed significant increases in permeability with several of the organic fluids studied". This was consistent with results found by Brown and Thomas [9] with commercially available clays and six solvents and petroleum products.

The objectives of this study was to (1) measure permeability of four organic solvents and water in soil; (2) evaluate the correspondence of water

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permeability to that of organic solvents; and (3) present a statistical model to determine soil permeability to solvents.

MATERIALS AND METHODS

Eight soils representative of four major orders (Alfisol, Aridisol, Entisol and Mollisol) were chosen (see Table 1). Only subsurface soil samples were used in order to minimize the effects of the natural organic matter. A wide range of physical and chemical characteristics are represented [2].

TABLE 1.

Characteristics of Soils Used.

Soil Name	Clay %	Silt %	Soil Paste pH	Cation Exchange Capacity (meq/100g)	Electrical Conductivity of Saturated Extract ($dS\ m^{-1}$)	Column Bulk Density ($Mg\ m^{-3}$)	Soil Surface Area ($m^2\ kg^{-1} \times 10^{-3}$)	Predominant Clay Minerals
Lake Bottom Clay (Entisol)	70.6	24.0	7.7	34.7	1.110	1.52	142	Illite Kaolinite
Nicholson (Alfisol)	49.0	47.0	6.7	37.0	0.176	1.53	120	Vermiculite
Fanno (Alfisol)	46.0	19.0	7.0	33.0	0.392	1.48	122	Montmorilonite Mica
Chalmers (Mollisol)	31.0	52.0	6.6	22.0	0.288	1.53	95.6	Montmorilonite Vermiculite
Canelo (Alfisol)	28.0	38.6	5.6	5.76	0.340	1.72	35.0	Kaolinite
Anthony (Entisol)	15.0	14.0	7.8	10.0	0.328	1.87	49.8	Montmorilonite Mica
Mohave (Aridisol)	11.1	37.0	7.3	10.0	0.615	1.78	38.3	Mica Kaolinite
River Bottom Sand (Entisol)	1.0	2.0	7.2	2.0	0.210	1.80	3.6	Kaolinite Mica

Organic liquids (solvents) used extensively by the chemical industry were chosen: Kerosene, isopropyl alcohol, xylene and ethylene glycol. Water was also used. Their properties are summarized in Table 2.

TABLE 2.

Properties of Solvents Used.

Solvent	Chemical Composition	μ-Viscosity[a] ($g\ s^{-1}\ m^{-1}$)	ρ-Density[a] ($Mg\ m^{-3}$)	Dielectric Coefficient	Properties
Xylene	$C_6H_4(CH_3)_2$	0.68[b,c]	0.8685[b,c]	2.4	Low polar Alkane immiscible Aromatic - aliphatic
Kerosene	$C_{12} - C_{18}$	2.42	0.82[b,c]	2.5	Nonpolar - alkane immiscible aromatic - aliphatic
Isopropyl Alcohol	C_3H_7OH	2.30	0.7854	18.0	Aliphatic polar, miscible
Ethylene Glycol	CH_2OHCH_2OH	23.0	1.1135	37.0	Aliphatic polar, miscible
Water	H_2O	1.0050	0.9982	80.0	

a. μ, ρ at 20°C
b. estimate
c. obtained data from manufacturer

Saturated hydraulic conductivity values were measured for all eight soils with each individual liquid following the procedure outlined by Klute [10]. All soils were air dried, crushed and sieved. Glass and plastic cylinders 5-8 cm in diameter and 25 cm long were used. Air-dry soil was packed in approximately 1 cm lifts to a depth of 5 cm to a uniform bulk density (Table 1).

A galvanized screen glued to the cylinder along with a 100 mesh brass strainer and two layers of fiberglass cloth ensured no loss of fine soil particles. Samples were left to soak in the appropriate liquid overnight and then an additional 6 cm of liquid added to the cylinder without disturbing the soil surface. The time necessary for the solvent to drop within 2 cm of the initial soil surface was recorded. Experiments were repeated until a constant hydraulic value was attained (within 5%), usually within two runs. Length of runs varied between 1.5 minutes for xylene in the Fanno to several weeks for ethylene glycol in Chalmers and Nicholson soils. A total of 211 columns were used. Most solvent-soil combinations were completed with six replications, although some were with as few as three.

The saturated hydraulic conductivity was calculated using the falling head equation:

$$K = (L/t) \ln[(H_1 + L)/(H_2 + L)]$$

where

L = length of soil sample
H_1 = initial depth of solvent
H_2 = final depth of solvent
t = time for head to drop from H^1 to H^2
K = hydraulic conductivity (length/time).

To compare the liquids, the intrinsic permeability was calculated using the equation

$$k = K\mu/\rho g$$

where

k = intrinsic permeability (m^2)
μ = viscosity ($kg\ m^{-1}\ s^{-1}$)
ρ = density ($Mg\ m^{-3}$)
g = the gravitational acceleration constant ($9.8\ m\ s^{-2}$)

If there were no soil-solvent interaction, then k would be independent of the liquid used.

RESULTS

The experimental means of the steady values of the hydraulic conductivity and intrinsic permeability are given for each soil-solvent combination in Table 3. Also included is the standard deviation (S.D.) of the replications. The soils are arranged in order of descending clay percentages and the solvents in order of increasing dielectric coefficients from left to right. The term "intrinsic permeability" follows the usual convention. The fact that its value differs according to solvent is not surprising, but merely confirms that the soils and solvents interact. (The more qualitative term "permeability" can also be used to denote either intrinsic permeability or hydraulic conductivity).

The intrinsic permeability varies inversely with the dielectric coefficient of the solvent. The only exceptions are with kerosene and xylene on the last 2 soils, but these solvents have nearly the same dielectric coefficients (2.5 and 2.4, respectively). The relationship between intrinsic permeability and dielectric coefficient is illustrated by Figure 1 for the sand, Anthony sandy loam Nicholson silty clay. The sand is relatively inert and the intrinsic permeability values are, for practical purposes, the same for all of the liquids. The Anthony has a considerably higher active fraction and the differences with the dielectric constant are more pronounced. For Nicholson, which is nearly 96% clay and silt, the differences between solvents are extreme. Correlation coefficients between log k and the dielectric coefficients are -0.56 for the sand,

TABLE 3

Experimental Means and Standard Deviations of Intrinsic Permeability for All Soil-Solvent Combinations.

Solvent	Soil						
	Lake Bottom Clay	Nicholson	Fanno	Chalmers	Canelo	Anthony	River Bottom Clay
Xylene							
K ($cm\ h^{-1}$)	6.11	1.26	64.5	0.625	0.522	1.59	66.6
k ($m^2 x10^{13}$)*	14.0	2.87	146.	1.42	1.19	3.63	151.
S.D.	1.42	0.217	38.2	0.211	0.193	0.727	43.6
Kerosene							
K ($cm\ h^{-1}$)	1.21	0.341	18.8	0.138	0.203	0.731	121.
k ($m^2 x10^{13}$)	10.1	2.85	157.	1.16	1.69	6.12	179.
S.D.	2.50	0.493	24.8	0.219	0.209	1.69	42.3
Isopropyl Alcohol							
K ($cm\ h^{-1}$)	0.771	0.082	11.2	0.084	0.126	0.342	21.
k ($m^2 x10^{13}$)	6.40	0.682	93.2	0.696	1.05	2.84	177.
S.D.	0.833	0.117	24.5	0.129	0.160	0.588	29.5
Ethylene Glycol							
K ($cm\ h^{-1}$)	0.041	$2.43x10^{-3}$	1.07	$6.47x10^{-3}$	$4.99x10^{-3}$	0.021	2.31
k ($m^2 x10^{13}$)	2.37	0.142	62.8	0.378	0.292	1.22	135.
S.D.	1.16	0.022	37.9[a]	0.068	0.018	0.402[a]	40.2
Water							
K ($cm\ h^{-1}$)	0.179	0.015	0.546	0.066	0.018	0.358	60.0
k ($m^2 x10^{13}$)	0.509	0.043	1.55	0.187	0.051	1.02	145.
S.D.	0.075	0.008	0.739	0.054[b]	0.015	0.121	20.7

Organic liquid combinations done with six replicates
Water combinations done with three replicates
[a] Five replicates
[b] Two replicates
*k values are 10^{-13} times the table entry

-0.89 for the Anthony and between -0.96 and -1 for all the other soils.

Multiple linear regression analyses were run with log k (for base 10) as the dependent variable following a forward, step-wise procedure. In the first set, the independent variables were silt, clay, bulk density and dielectric coefficient. In the second set, the log k determined with water was deleted as a dependent variable, but included as an independent variable describing the soil. The forward step-wise procedure was performed by selecting for each step the unused variable having the greatest absolute value of the computed partial correlations. (The analysis was by the statistical program "Daisy Professional", Rainbow Computing, Inc., 8811 Amigo Ave., Northridge, CA 91324)*. For the first set using all liquids, the most significant variable is "% silt" resulting in an R (goodness of fit) of 0.57. That % silt is more significant than the % clay or % sand is not surprising in that the textural classes are interdependent, and the most significant class definitely does not indicate a causal effect. When the dielectric coefficient was added, this became R = 0.64 and when % clay and bulk density were added, it became R = 0.74.

* Not an endorsement, but for reader's information.

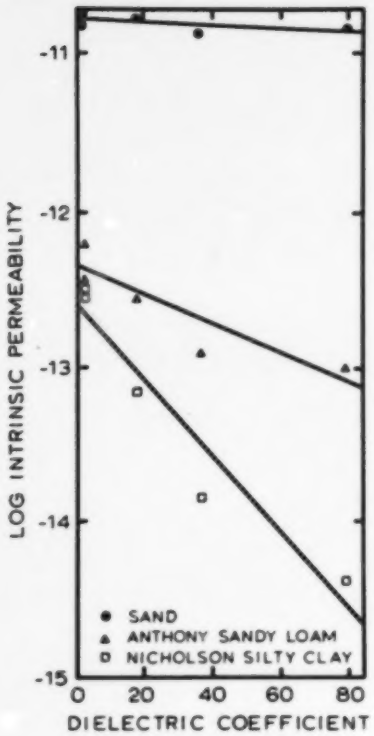

FIGURE 1. Relationship of coefficient and intrinsic permeability of soil. The values for k are from Table 3.

For the second analysis, the log k_{water} as a lone independent variable gave an R of 0.84. When the dielectric constant and silt were added the R became 0.85.

DISCUSSION

The results point out the extent of variation in the intrinsic permeability due to interactions of the liquid and soil. The electrical-double-layer model is useful to explain variation in intrinsic permeability for a particular soil due to the effects of a polar liquid. A concise explanation of the double layer theory is by Bohn et al. [11]. As the dielectric constant increases, the attractive force between opposing charges decreases, initiating an expansion of the double layer (dispersion) and reducing the intrinsic permeability of the soil. If this mechanism governs the flow of liquids in a soil, the higher the dielectric constant of a liquid, the lower would be the permeability to that liquid. This effect can be seen clearly in Table 3 and is most prevalent for soils containing high amounts of clay. The results are compatable with those of Brown and Thomas [9] who found "dramatic increases in conductivity over the corresponding permeabilities to water."

TABLE 4.

Coefficients resulting from linear regression analyses for log k (units of k are m^{-2}) (the "log" is for base 10).

1. All liquids		
a.	$\log k = -11.2 - 0.0380$ (% silt)	(R = 0.57)
b.	$\log k = -10.9 - 0.0380$ (% silt) $- 0.0110$ (dielectric coef.)	(R = 0.64)
c.	$\log k = -10.7 - 0.0340$ (% silt) -0.0110 (dielectric coef.) $- 0.00908$ (% clay)	(R = 0.67)
d.	$\log k = -1.63 - 0.0448$ (% silt) $- 0.0110$ (dielectric coef.) $- 0.0338$ (% clay) $- 4.86$ (B.D.)	(R = 0.74)
2. All liquids except water		
a.	$\log k = 0.894 + 0.701 \log k_{water}$	(R = 0.84)
b.	$\log k = 0.890 + 0.701 \log k_{water} - 0.000163$ (dielectric coef.)	(R = 0.84)
c.	$\log k = 1.10 + 0.636 \log k_{water} - 0.000163$ (dielectric coef.) $- 0.000756$ (% silt)	(R = 0.85)

Green et al. [12] concluded, on the contrary, that the permeability of liquids increased with dielectric constant. A major difference in their experiments was that the soil was initially wetted with water. Thus, their conditions included the complication of a water-organic liquid phase boundary. Such a phase boundary would have persisted longer, and acted as a barrier, for the less-miscible, low dielectric liquids. The intrinsic permeability of these liquids would only have become obvious late in their experiment and may have accounted, in part, for observations by Green et al. [12] that "A number of the systems clearly showed anomalous behaviour with respect to permeability-dielectric constant relationship."

For initially air-dried soils that have been wetted with a particular solvent and achieved a steady state, the mechanism that presumably will govern the flow of that particular liquid is that of the double electric layer. Thus the intrinsic permeability will vary depending on the soil itself and the polarity of the liquid as related by its dielectric constant. These relationships are expressed by the regression equations of Table 4. The regression results apply particularly for the soils and solvents studied and should be a reasonable approximation for other similar soils and liquids.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement CR-810268 to The University of Arizona, it has not been subjected to the Agency's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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